

Effect of A -site size difference on polar behavior in $MBiScNbO_6$, ($M=Na, K$ and Rb): Density functional calculations

Shigeyuki Takagi^{1,2}, Alaska Subedi^{1,2}, Valentino R. Cooper¹, and David J. Singh¹
¹*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6114*
²*Department of Physics, University of Tennessee, Knoxville, TN 37996*
 (Dated: August 18, 2010)

We investigate the effect of A -site size differences in the double perovskites $BiScO_3-MNbO_3$ ($M=Na, K$ and Rb) using first-principles calculations. We find that the polarization of these materials is $70\sim 90 \mu C/cm^2$ along the rhombohedral direction. The main contribution to the high polarization comes from large off-centerings of Bi ions, which are strongly enhanced by the suppression of octahedral tilts as the M ion size increases. A high Born effective charge of Nb also contributes to the polarization and this contribution is also enhanced by increasing the M ion size.

PACS numbers: 77.84.Ek, 71.20.Ps

I. INTRODUCTION

Ferroelectric perovskite oxides have attracted attention for many years because of their many applications in technology, including memory devices, electronic components, piezoelectric sensors and actuators, and pyroelectric devices.¹ Besides the technological importance, there is also a great scientific interest in understanding the underlying physics. This is stimulated by recent discoveries of entirely new ferroelectrics particularly in thin film form.²⁻⁴ The key to these materials is competition between different interactions, leading to structural instability. Ferroelectricity in perovskite ABO_3 oxides depends on the delicate balance of the long-range Coulomb energy, which favors a ferroelectric distortion, and the short-range ionic repulsion, which stabilizes the cubic phase.^{5,6} More generally, instabilities in perovskites are often discussed in terms of competition between preferred A -O and B -O bond lengths, which cannot both be accommodated in the ideal cubic structure for arbitrary A and B ions. This is characterized by a so-called tolerance factor, t , that describes the degree of non-satisfaction of ideal bond lengths in the cubic perovskite structure. The balance between the long-range Coulomb energy and short-range ionic repulsion can be modified by smaller effects related to the A -O hybridization, in particular the so-called lone pair physics associated with stereochemically active ions, particularly Pb^{2+} and Bi^{3+} , as in the technologically important $Pb(Zr,Ti)O_3$ system and $BiFeO_3$. In thin films and superlattices the constraint imposed by lattice matching imposes strains that push bond lengths away from their ideal values, leading to highly enhanced ferroelectric instabilities in many cases.^{3,4,7}

The piezoelectric performance in perovskite ferroelectrics is associated with polarization rotation near morphotropic phase boundaries (MPB).⁸⁻¹³ That is, in materials where two different ferroelectric states with different lattice strains are close in energy, an electric field may rotate the polarization and therefore the ferroelectric state from the zero field equilibrium configuration towards the other nearby configuration, with resulting

coupling to the lattice strain. Strong ferroelectricity is highly desirable for piezoelectricity, but epitaxial constraints on the lattice strain as in most thin films are not. It is of interest to examine strategies for producing structural frustration and perhaps enhance ferroelectricity in bulk materials.

In this regard, recent first principles calculations suggest that A -site off-centering can be enhanced by the use of ions with different ionic radii at the A -site.¹⁴ There is experimental support for this in the $(Ba,Ca)TiO_3$ solid solution, which shows a strongly stabilized ferroelectric tetragonal phase over a wide composition range as compared to what would be expected from a classical averaging of the end-point properties.¹⁵ However, while this is shown experimentally to be effective in enhancing ferroelectricity in $(Ba,Ca)TiO_3$ it is not effective in the closely related $(Ba,Ca)ZrO_3$ system.¹⁶ We recently reported results of a first principles study of the double perovskites, $BiPbZnNbO_6$ and $BiSrZnNbO_6$, which have a large size difference on the A -site.¹⁷ We found high polarization values of $\sim 80 \mu C/cm^2$ in these compounds, which is comparable to $BiFeO_3$ ($90-100 \mu C/cm^2$)¹⁸ even though these double perovskites have only half the A -sites occupied by the stereochemically active Bi^{3+} ion. The high polarization in these materials results comes from large off-centerings of Bi ions, associated in part with the A -site size mismatch, cooperating with moderate off-centerings of Nb ions that have Born effective charges highly enhanced by covalency.

Here we use density functional calculations to study the double perovskites $MBiScNbO_6$ ($M = Na, K$ and Rb) in order to further investigate the effect of A -site size differences on the polar behavior of perovskites. In relation to $BiSrZnNbO_6$, the compounds that we study here have lower ionic charges at the A -site and higher ionic charges at the B -site. The M ions have increasing ionic radii ($r_{Na^+} < r_{K^+} < r_{Rb^+}$), but are otherwise chemically similar, which is helpful in understanding how increasing A -site size difference affects the ferroelectricity. Finally, we note that these materials could potentially be of practical use. It is known that the end-point compound $BiScO_3$ (BS) strongly favors a rhombohedral

state over a tetragonal state,^{19–21} as does BiSrZnNbO₆. As such these systems, when alloyed with a tetragonal ferroelectric can show MPBs and possibly form useful piezoelectrics.¹⁹

II. APPROACH

We investigated the lattice instabilities of three perovskite oxides (Na,Bi)(Sc,Nb)O₆, (K,Bi)(Sc,Nb)O₆ and (Rb,Bi)(Sc,Nb)O₆ using density functional theory (DFT) within the local-density approximation (LDA). All calculations, including the structure relaxations, polarizations and Born effective charges, were done using a plane wave basis as implemented in Quantum Espresso package.²² We used ultrasoft pseudopotentials²³ and converged our results with respect to the cut-off energy and Brillouin zone sampling, similar to our previous study for BiPbZnNbO₆ and BiSrZnNbO₆.¹⁷ The polarization was calculated using the Berry's phase method.

There is a large charge difference between Sc³⁺ and Nb⁵⁺, and this is expected lead to a strong ordering tendency on the *B*-site. This is actually the case in the relaxor compound PbSc_{1/2}Nb_{1/2}O₃ (PSN), where Sc and Nb have rock-salt ordering.^{24,25} Here we consider material with this double perovskite type *B*-site ordering. In addition, while ordering at the *A*-site is less clear, there is a large charge difference at the *A*-site, which may lead to an ordering tendency at least short range, as well. There have been reports of short-range cation ordering of Na⁺ or K⁺ and Bi³⁺ in Na_{1/2}Bi_{1/2}TiO₃ (NBT) and K_{1/2}Bi_{1/2}TiO₃ (KBT),^{26–29} which support this view. Here we consider the ordered system, both because it is simpler, which facilitates the calculations and analysis, and because it helps to avoid computational artifacts, such as polarization because of the particular symmetry breaking chemical ordering in a given supercell.

There are various factors at play that may drive ferroelectricity in NaBiScNbO₆ (NBSN), KBiScNbO₆ (KBSN) and RbBiScNbO₆ (RBSN). These materials have Nb⁵⁺ at the *B*-site which favors ferroelectricity, as in KNbO₃. The end-point perovskite BiScO₃ has a very small tolerance factor $t = 0.85$ and a stereochemically active Bi³⁺ at the *A*-site, two factors that are considered to be important in *A*-site driven materials, leading to strong lattice instabilities. Furthermore, the large size difference at *A*-site may also enhance the off-centering of the *A*-site ions through frustration of tilt modes. However, in addition to *A*-site off-centering, low tolerance factors also strongly favor rotation of the *BO*₆ octahedra. These rotations compete with ferroelectricity in general. In order to sort this out it is important to use supercells that have even numbers of units along the [100], [010] and [001] directions to accommodate the various Glazer tilt patterns.³⁰ We used 40 atom 2×2×2 supercells and assumed both *A*- and *B*-site rocksalt chemical ordering. In addition to allowing various Glazer tilt patterns, these supercells are cubic and therefore non-polar as regards

to chemical ordering. Thus, any off-centering is a consequence of lattice instabilities and not an artifact due to cation ordering in the supercell.

III. RESULTS AND DISCUSSION

To our knowledge, syntheses of NaBiScNbO₆, KBiScNbO₆ and RbBiScNbO₆ have not been reported. We therefore used theoretical LDA lattice parameters. We note that in oxides with heavy elements the LDA typically leads to a small underestimation of the lattice parameter by ~ 1 -2%. If this is the case here, it will work against ferroelectricity and in favor of competing tilt instabilities.³¹ We assume a pseudocubic structure to evaluate the lattice parameters and relaxed all atomic coordinates with no symmetry constraints. This was done as a function of the lattice parameter to find the equilibrium volumes for these materials. The calculated LDA lattice parameters for the minimum energy were 3.98 Å, 4.03 Å and 4.07 Å for NaBiScNbO₆, KBiScNbO₆ and RbBiScNbO₆, respectively. These show the expected trend with increase in the *A*-site ion size.

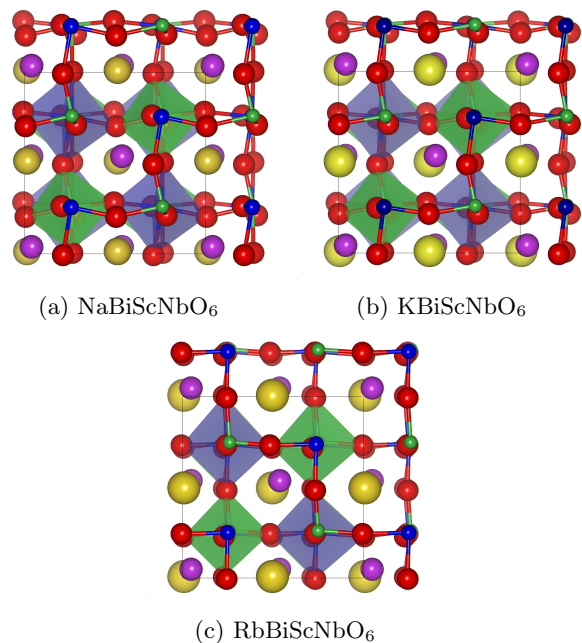


FIG. 1: (color online) Projections onto a (010) plane of the structures of the relaxed 40 atom pseudocubic (a) NaBiScNbO₆, (b) KBiScNbO₆ and (c) RbBiScNbO₆ supercells. The *B*-O bonds are shown. The Bi ions are denoted by light purple spheres, the Sc ions by blue, the Nb ions by light green, and the O ions by red. The Nb, K and Rb ions are shown by dark yellow spheres in each panel. The O octahedra for Sc are shown by (semi-transparent) blue boxes and those for Nb by (semi-transparent) green. The solid lines show the unit cell boundaries of each material.

Fig. 1 shows the structures of the relaxed 40 atom pseudocubic NaBiScNbO₆, KBiScNbO₆ and RbBiScNbO₆ su-

percells at the equilibrium volume. As expected, the octahedral tilting is reduced with larger A -site ion size difference (note that the ionic radii of A -site ions are $r_{\text{Bi}^{3+}} = 1.31 \text{ \AA}$, $r_{\text{Na}^+} = 1.53 \text{ \AA}$, $r_{\text{K}^+} = 1.78 \text{ \AA}$ and $r_{\text{Rb}^+} = 1.86 \text{ \AA}$, respectively). In particular, there is relatively little tilt in RbBiScNbO_6 , which has the largest A -site size difference. Fig. 1 also shows large displacements of the Bi ions from the ideal positions at the centers of the O cages.

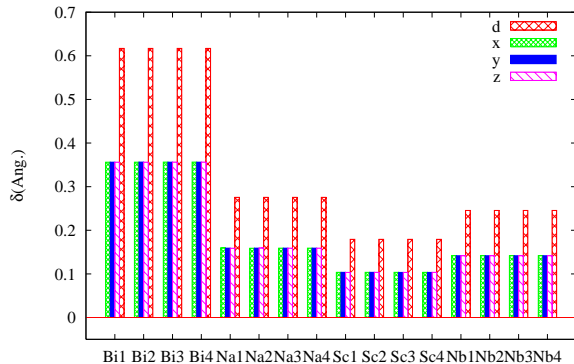


FIG. 2: (color online) Cation off-centerings along the Cartesian directions and their magnitude with respect to the center of their O cages (the 12 nearest O ions for the A -site and the 6 nearest for the B -site) in the relaxed 40 atom NaBiScNbO_6 supercell.

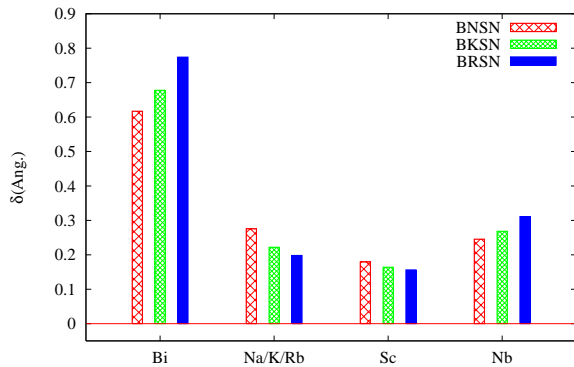


FIG. 3: (color online) Average magnitude of cation off-centerings with respect to the center of their O cages in the relaxed 40 atom NaBiScNbO_6 , KBiScNbO_6 and RbBiScNbO_6 supercells.

The cation off-centerings in NaBiScNbO_6 from the center of their O cages is shown in Fig. 2. All cations off-center along $[111]$ direction and the magnitude of displacement is almost the same for a given cation. The Bi ions have a large off-centering, which is a consequence of the difference in size compared to the other A -site ion and also its stereochemical activity. In addition to the off-centering of A -site cations, there are displacements of B -site cations as well. For NaBiScNbO_6 , the average magnitudes of the cation off-centerings are

0.62 \AA for Bi^{3+} , 0.28 \AA for Na^+ , 0.18 \AA for Sc^{3+} and 0.24 \AA for Nb^{5+} , respectively. This cooperation of all cations in the ferroelectric distortion is not unusual and is also seen in KNbO_3 , BaTiO_3 , PbTiO_3 , BiPbZnNbO_6 and BiSrZnNbO_6 .^{17,32,33} The cation off-centerings in KBiScNbO_6 and RbBiScNbO_6 are also collinear along $[111]$ direction.

As mentioned, the LDA lattice parameters of these supercells may be underestimated by 1-2%. To study the robustness of ferroelectric displacements, we performed relaxation calculations for larger values of lattice parameters that lie between the equilibrium lattice parameters (3.98 \AA , for NaBiScNbO_6 , 4.03 \AA , for KBiScNbO_6 and 4.07 \AA , for NaBiScNbO_6) and the higher value of 4.23 \AA . We found ferroelectric cation off-centerings for each such calculation, confirming the robustness of ferroelectric distortions against LDA volume errors.

Fig. 3 shows the average magnitudes of the cation off-centerings in NaBiScNbO_6 , KBiScNbO_6 and RbBiScNbO_6 . The displacements of Bi and Nb increase as the A -site size difference is increased. The reason for this increase in displacement is two-fold. First, the larger size difference decreases the tilting of BO_6 octahedra and provides more volume for displacement of Bi and Nb ions. Secondly, the lattice parameter increases as the size of M ion increases. The ferroelectricity becomes stronger with increasing volume, as is usual in perovskite oxides.³⁴ Competing with this is the fact that, since polarization is dipole per unit volume, larger unit cell volume works against high polarization. It is interesting to note that in contrast to Bi and Nb ions, the off-centerings become smaller for the M ions, while there is no appreciable change in the displacement of Sc ion. As discussed below, there is little covalency between the unoccupied states of the M ions with the occupied O $2p$ states in these materials. This works against off-centering. Furthermore, $r_{\text{Na}^+} < r_{\text{K}^+} < r_{\text{Rb}^+}$, and as the radius of an atom increases, there is less volume available for off-centering. This explains the smaller displacement of Rb ions as compared to Na ions.

We now consider the electronic structure of these materials as it pertains to ferroelectricity. Fig. 4 shows the electronic density of states (DOS) of the pseudocubic relaxed NaBiScNbO_6 and the projections onto Bi p , Sc d , Nb d and O p pseudo-wavefunctions (the DOS of KBiScNbO_6 and RbBiScNbO_6 are almost identical and are not shown here). The O $2p$ states provide the DOS from -5 eV to the valence band maximum and there is a gap that separates the O $2p$ derived states from the unoccupied metal states. The calculated LDA band gap is 3.2 eV , 3.1 eV and 3.1 eV for NaBiScNbO_6 , KBiScNbO_6 and RbBiScNbO_6 , respectively. The actual band gaps are likely to be larger than these calculated ones due to LDA band gap underestimation. In any case, based on the calculated gaps, these materials are expected to be good insulators at ambient temperature. The O $2p$ derived valence bands contain significant admixtures of the nominally unoccupied metal states, which are mainly of

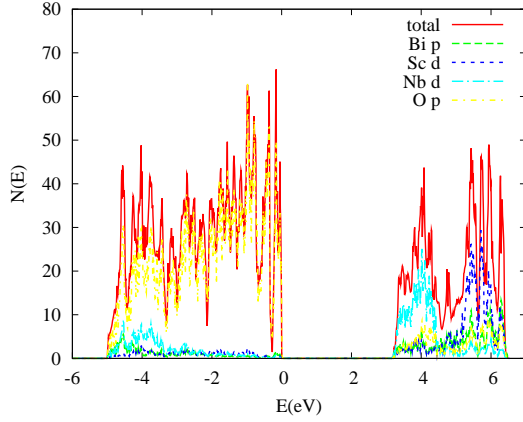


FIG. 4: (color online) Electronic DOS of the pseudocubic relaxed NaBiScNbO₆ and the Bi *p*, Sc *d*, Nb *d* and O *p* projections. The valence band maximum is taken as the energy zero.

Bi 6*p*, Sc 3*d* and Nb 4*d* character. This mixing of occupied O 2*p* states with unoccupied *d* states of metals implies chemical bonding and is responsible for enhanced Born effective charges and ferroelectric off-centering, as in PbTiO₃ and BaTiO₃.^{6,35} Nb 4*d* states are dominant near the conduction band minimum and this low energy favors hybridization with O 2*p* states, as discussed in the case of PbMg_{1/3}Nb_{2/3}O₃ and KNbO₃ in comparison with KTaO₃.^{36,37} However, the Sc 3*d* states lie further above the conduction band minimum and this results in a somewhat weaker hybridization with O 2*p* states. We do not find significant mixing of unoccupied Na/K/Rb *s* states with the occupied O 2*p* states as may be expected considering the very large electronegativity difference between these elements and O. In NBSN, the influence of covalency is reflected in the enhanced Born effective charges of 4.38 for Bi, 4.73 for Sc and 6.42 for Nb as compared to the very modest enhancement of ($z^*=1.14$) for Na. Similar numbers are obtained for KBSN and RBSN (see Table I).

In contrast to the trend in the cation off-centerings, the Born effective charges of Bi and Nb decrease, while those of *M* and Sc ions increase when the *A*-site size difference becomes larger. These decreases in Born charges of Bi and Nb ions would mean lower values of polarization if the Born charges were independent of atom position and the off-centering were of the same magnitude in all compounds. In fact, however, the polarizations as calculated with the Berry phase method are 73 $\mu\text{C}/\text{cm}^2$ for NBSN, 77 $\mu\text{C}/\text{cm}^2$ for KBSN, and 87 $\mu\text{C}/\text{cm}^2$.

As mentioned, high piezoelectric performance is induced by the polarization rotation from the rhombohedral state to tetragonal state near the MPB. We studied the tendency towards tetragonality by calculating the total energies of NBSN, KBSN, and RBSN as a function of imposed tetragonal strain ($0.94 < c/a < 1.06$) while keeping the volumes equal to their equilibrium volume for the pseudocubic cells. In all materials, the lowest en-

TABLE I: Comparison of properties of NaBiScNbO₆, KBiScNbO₆ and RbBiScNbO₆, where r_{M+} denotes the ion radii of *M* ion, *a* denotes the pseudocubic lattice parameter, z^* denotes the average Born effective charge, δ denotes the average cation off-centering with respect to the O cages, and *P* is the magnitude of polarization.

	NaBiScNbO ₆	KBiScNbO ₆	RbBiScNbO ₆
r_{M+} (Na/K/Rb)	1.53 Å	1.78 Å	1.86 Å
<i>a</i> (LDA)	3.98 Å	4.03 Å	4.07 Å
δ (Bi)	0.62 Å	0.67 Å	0.77 Å
z^* (Bi)	4.38	4.21	3.73
δ (Na/K/Rb)	0.28 Å	0.22 Å	0.20 Å
z^* (Na/K/Rb)	1.14	1.17	1.22
δ (Sc)	0.18 Å	0.16 Å	0.16 Å
z^* (Sc)	4.73	4.81	4.92
δ (Nb)	0.24 Å	0.27 Å	0.31 Å
z^* (Nb)	6.42	6.23	5.80
<i>P</i> (111)	73 $\mu\text{C}/\text{cm}^2$	77 $\mu\text{C}/\text{cm}^2$	87 $\mu\text{C}/\text{cm}^2$

ergy is at $c/a = 1.00$ and the cation off-centerings are collinear and along [111] direction. The cations do not off center along [001] directions even with large c/a and the off-centerings remain practically along the [111] direction over the range of c/a values that we tried, implying robustness of the rhombohedral ferroelectricity. Therefore, these are rhombohedral ferroelectric materials, and as such it is of interest to alloy with tetragonal ferroelectrics in order to produce a potential MPB.

Related to this, a similar compound Na_{0.5}Bi_{0.5}TiO₃ (NBT) is also a rhombohedral ferroelectric³⁸ with $T_C = 593.15$ K and polarization 38 $\mu\text{C}/\text{cm}^2$.³⁹ Solid solutions of NBT with tetragonal BaTiO₃ (NBBT) show a useful MPB with polarization 20 $\mu\text{C}/\text{cm}^2$.³⁹ While the material has not proved superior to other compounds such as Pb(Zr,Ti)O₃ in transducers, it does have a lower free permittivity and a high electromechanical coupling factor that make it an interesting lead-free actuator material. The materials in the present study are similar in that they are rhombohedral ferroelectrics and may be considered to be related to NBT with Ti replaced by Sc_{0.5}Nb_{0.5}. By analogy, solid solutions of these materials with BaTiO₃ may provide materials that are useful as lead-free piezoelectrics. Another possibility may be alloying with the super tetragonal material Bi(Zn,Ti)O₃.⁴⁰

IV. CONCLUSIONS

We investigated the polar behavior of double perovskites NaBiScNbO₆, KBiScNbO₆ and RbBiScNbO₆ using density functional calculations on small supercells. We find high polarization along [111] directions. The main contribution to the polarization comes from large displacements of Bi and more modest displacements of Nb ions, which, however, have high Born charges. We find that the polarization increases as the *A*-site size difference becomes larger. These materials also have sub-

stantial band gaps and the rhombohedral ferroelectricity is robust. It will be of interest to investigate whether solid solutions of these materials with tetragonal ferroelectrics show MPBs possibly providing another avenue for development of lead-free piezoelectrics.

Acknowledgements

This work was supported by the Materials Sciences and Engineering Division, Office of Basic Energy Sci-

ences, U.S. Department of Energy (AS,VRC,DJS) and the Office of Naval Research (ST).

-
- ¹ J. F. Scott, *Science* **315**, 954 (2007).
 - ² C. H. Ahn, K. M. Rabe, and J. M. Triscone, *Science* **303**, 488 (2004).
 - ³ H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, and D. H. Lowndes, *Nature (London)* **433**, 395 (2005).
 - ⁴ M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* **77**, 1083 (2005).
 - ⁵ R. E. Cohen and H. Krakauer, *Phys. Rev. B* **42**, 6416 (1990).
 - ⁶ R. E. Cohen, *Nature* **358**, 136 (1992).
 - ⁷ V. R. Cooper and K. M. Rabe, *Phys. Rev. B* **79**, 180101 (2009).
 - ⁸ S.-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
 - ⁹ B. Noheda, D. E. Cox, G. Shirane, L. E. Cross, and Z. Zhong, *Appl. Phys. Lett.* **74**, 2059 (1999).
 - ¹⁰ L. Bellaiche, A. Garcia, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5427 (2000).
 - ¹¹ H. Fu and R. E. Cohen, *Nature* **403**, 281 (2000).
 - ¹² R. Guo, L. E. Cross, S.-E. Park, B. Noheda, D. E. Cox, and G. Shirane, *Phys. Rev. Lett.* **84**, 5423 (2000).
 - ¹³ B. Noheda, D. E. Cox, G. Shirane, S.-E. Park, L. E. Cross, and Z. Zhong, *Phys. Rev. Lett.* **86**, 3891 (2001).
 - ¹⁴ D. J. Singh and C. H. Park, *Phys. Rev. Lett.* **100**, 087601 (2008).
 - ¹⁵ D. Fu, M. Itoh, S. Y. Koshihara, T. Kosugi, and S. Tsuneyuki, *Phys. Rev. Lett.* **100**, 227601 (2008).
 - ¹⁶ H. S. Kim, H. M. Christen, M. D. Biegalski, and D. J. Singh, *J. Appl. Phys.* **108**, in press (2010).
 - ¹⁷ S. Takagi, A. Subedi, D. J. Singh, and V. R. Cooper, *Phys. Rev. B* **81**, 134106 (2010).
 - ¹⁸ J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Phys. Rev. B* **71**, 014113 (2005).
 - ¹⁹ R. E. Eitel, S. J. Zhang, T. R. Shrout, C. A. Randall, and I. Levin, *J. Appl. Phys.* **96**, 2828 (2004).
 - ²⁰ J. Iniguez, D. Vanderbilt, and L. Bellaiche, *Phys. Rev. B* **67**, 224107 (2003).
 - ²¹ S. V. Halilov, M. Fornari, and D. J. Singh, *Phys. Rev. B* **69**, 174107 (2004).
 - ²² S. Baroni, A. dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, et al., URL <http://www.quantum-espresso.org>.
 - ²³ D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
 - ²⁴ F. Chu, I. M. Reaney, and N. Setter, *J. Appl. Phys.* **77**, 1671 (1995).
 - ²⁵ C. Malibert, B. Dkhil, J. M. Kiat, D. Durand, J. F. Béarar, and A. Spasojevic-de Biré, *J. Phys.: Condens. Matter* **9**, 7485 (1997).
 - ²⁶ S.-E. Park, S.-J. Chung, I.-T. Kim, and K. S. Hong, *J. Am. Ceram. Soc.* **77**, 2641 (1994).
 - ²⁷ G. O. Jones, J. Kreisel, and P. A. Thomas, *Powder Diffr.* **17**, 301 (2002).
 - ²⁸ G. O. Jones and P. A. Thomas, *Acta Crystallogr. B* **58**, 168 (2002).
 - ²⁹ J. Petzelt, S. Kamba, J. Febry, D. Noujni, V. Porokhonskyy, A. Pashkin, I. Franke, K. Rolder, J. Suchniz, R. Klein, et al., *J. Phys.: Condens. Matter* **16**, 2719 (2004).
 - ³⁰ A. M. Glazer, *Acta Crystallogr. Sect. B* **28**, 3384 (1972).
 - ³¹ M. Fornari and D. J. Singh, *Phys. Rev. B* **63**, 092101 (2001).
 - ³² D. J. Singh and L. L. Boyer, *Ferroelectrics* **136**, 95 (1992).
 - ³³ M. Ghita, M. Fornari, D. J. Singh, and S. V. Halilov, *Phys. Rev. B* **72**, 054114 (2005).
 - ³⁴ G. Samara and P. Peercy, *Solid State Physics-Advances In Research And Applications* **36**, 1 (1981).
 - ³⁵ W. Zhong, R. D. King-Smith, and D. Vanderbilt, *Phys. Rev. Lett.* **72**, 3618 (1994).
 - ³⁶ D. J. Singh, *Phys. Rev. B* **53**, 176 (1996).
 - ³⁷ M. Suewattana and D. J. Singh, *Phys. Rev. B* **73**, 224105 (2006).
 - ³⁸ C. F. Buhrer, *J. Chem. Phys.* **36**, 798 (1962).
 - ³⁹ T. Takenaka, K. Maruyama, and K. Sakata, *Jpn. J. Appl. Phys.* **30**, 2236 (1991).
 - ⁴⁰ M. R. Suchomel, A. M. Fogg, M. Allix, H. J. Niu, J. B. Claridge, and M. J. Rosseinsky, *Chem. Mater.* **18**, 4987 (2006).